# STABILIZED TETRAFLUOROETHYLENE-FLUOROOLEFIN COPOLYMERS HAVING METHYL ESTER END-GROUPS AND PROCESS FOR PRODUCING SAME

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Abstract of **GB1231333**

1,231,333. Stabilized tetrafluoroethylene co- polymers. E.I. DU PONT DE NEMOURS & CO. 26 March, 1969 [1 April, 1968], No. 15960/69. Heading C3P. A copolymer of tetrafluoroethylene and another ethylenically unsaturated fluorine- substituted monomer in which, as measured by infra-red analysis, at least half of the end groups are of the formula and remaining end groups (if any) are radicals may be prepared by stabilizing such a copolymer having end groups of the formula by converting at least half of these end groups to methyl ester groups. In the examples tetra- fluoroethylene, perfluoropropylperfluorovinyl ether and hexafluoropropylene are copolymer- ized in the presence of 1,2,2-trichloro-1,1,2- trifluoroethane, bis(perfluoropropionyl)peroxide water and ammonium persulphate and treated with methanol.

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C3P 10D4A 10D5 10K10 10K6 10P1E3 10P1E5 10P2X 10P3 10P6A 10T2D 6D3 6K10 6P1E3 6P3 6P6A 6T2D

# (54) STABILISATION OF FLUORINE-CONTAINING POLYMERS

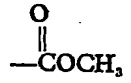
(71) We, E. I. Du Pont de Nemours and Company, a Corporation organised and existing under the laws of the State of Delaware, United States of America, of Wilmington 98, Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the stabilization of fluorine-containing polymers.

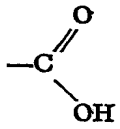
In general, fluorocarbon copolymers are known to have outstanding thermal stability. However, certain copolymers of tetrafluoroethylene (TFE) have a certain amount of instability introduced into the polymer in the initiation and termination steps of the polymerization. Both the initiation and termination of the chain can result in unstable end-groups, such as carboxylic acid end-groups and acid fluoride end-groups which on storage can be converted into carboxylic acid end-groups being present in the polymer molecule. During melt extrusion carboxylic acid groups degrade and form gases which in turn cause bubbles to form in the polymer.

United States Patent Specification No. 3,085,083 proposes that these unstable carboxylic acid and acid fluoride end-groups should be stabilized by a high-temperature humid heat treatment process. However, this humid heat-treatment process suffers from the disadvantages that it is very expensive to perform and thus adds considerably to the cost of the treated polymers and that the treated polymer tends to be contaminated with dust and other particles which may be introduced during the heat-treatment process.

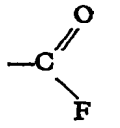
The present invention provides a stabilized copolymer of tetrafluoroethylene and another ethylenically unsaturated fluorine-substituted monomer in which, as measured by infra-red analysis, at least half of the end-groups are of the formula



and remaining end-groups (if any) are

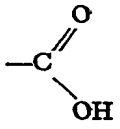


or

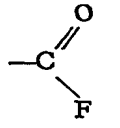


radicals.

These stabilized copolymers may be prepared from copolymers of tetrafluoroethylene and another ethylenically unsaturated fluorine-substituted monomer, which copolymer has end-groups of the formula



or



by a process which comprises converting at least half of said end-groups to methyl ester groups.

The methyl ester end-groups are quite stable under prolonged storage at extrusion

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temperatures and the electrical properties of polymers containing a large number of methyl ester end-groups have been found to be equivalent to those of polymers containing other stable end-groups such as —$CF_2H$.

Copolymers which may be used in the present invention include, for example, copolymers of TFE with hexafluoropropylene (HFP) or perfluoroalkyl perfluorovinyl ethers prepared in aqueous media using persulphate initiators and tetrafluoroethylene/perfluoroalkyl perfluorovinyl ether copolymers produced in non-aqueous media and thus containing acid fluoride end-groups.

Preferably the starting copolymers used in the present invention are the copolymers (prepared in either aqueous or non-aqueous media) or tetrafluoroethylene with a fluoroolefin having the general formula

$$XCF_2(CF_2)_nCF=CF_2$$

where X represents a fluorine or hydrogen atom and n is 0 or an integer from 1 to 9, such as hexafluoropropylene, perfluoropentene-1, and 8-hydroperfluorooctene-1; a fluorovinyl ether having the general formula

$$XCF_2(CF_2)_mOCF=CF_2$$

where X represents a fluorine or hydrogen atom and m is 0 or an integer from 1 to 7, such as perfluoromethyl perfluorovinyl ether, perfluoroethyl perfluorovinyl ether, perfluoropropyl perfluorovinyl ether, and 3-hydroperfluoropropyl perfluorovinyl ether; a fluorovinyl polyether having the general formula

$$XCF_2(CF_2)_mOCF(CF_3)CF_2OCF=CF_2$$

where X represents a fluorine or hydrogen atom and m is 0 or an integer from 1 to 7, or perfluoro(2 - methylene - 4 - methyl - 1,3 - dioxolane).

The carboxylic acid end groups and the acid fluoride end-groups of the TFE copolymers may readily be converted to methyl ester end-groups by contacting them with, for example, small amounts of methanol. A wide range of reaction conditions may be used to produce the desired ester end-groups. In general the higher the temperature and pressure used the quicker the esterification of polymers having carboxylic acid end-groups. Polymers having acid fluoride end-groups can normally be esterified by contacting the polymer with methanol at room temperature. Usually the temperature used for esterifying copolymers having acid fluoride (—COF) end-groups is from 0° to 200° C, preferably 20° C to 65° C. Similarly the esterification of copolymers having carboxylic acid (—COOH) end-groups is usually carried out at 65° to 200° C, preferably 130° to 200° C. These different temperature ranges are usually necessary because the copolymers produced in aqueous media, i.e. containing carboxylic acid end-groups are more difficult to esterify and thus require more strenuous heating than the copolymers produced in non-aqueous media which contain acid fluoride end-groups.

Thus, for example, tetrafluoroethylene copolymers produced by non-aqueous dispersion polymerization having acid fluoride end-groups can be effectively stabilized by (a) contacting said copolymers with methyl alcohol at temperatures from 0° to 200° C.; and then (b) recovering the methyl ester of the tetrafluoroethylene copolymer. Similarly tetrafluoroethylene copolymers produced by aqueous methods having carboxylic acid end-groups as a result thereof, can be stabilized with methyl alcohol using a temperature of 65° to 200° C.

The copolymers may be contacted with methanol by making a slurry of the starting copolymer in liquid methanol or by contacting the starting copolymer with methanol vapour. When the copolymer of TFE is prepared in a non-aqueous medium, the methanol may simply be added to a slurry of the copolymer in the solvent in which it was prepared. The copolymer is allowed to remain in contact with the methanol until at least half of the acidic end-groups of the copolymer have been converted to methyl ester end-groups.

While, due to its ready availability and low cost methanol is the preferred reagent for forming the methyl ester end-groups, other reagents, such as trimethyl orthoformate or trimethyl orthoacetate may also be used to effect this esterification. The esterifying reagent should be in molar excess to force the reaction to go toward the production of the ester of the TFE copolymer.

The existence and quantity of certain end-groups in the polymers generally was determined using the infrared spectrum obtained on compression moulded films of about 10 mils thickness. The end-groups of interest were found to absorb at 1883 $cm.^{-1}$, 1814 $cm.^{-1}$, 1800 $cm.^{-1}$, 1793 $cm.^{-1}$ and 1781 $cm.^{-1}$. The 1883 $cm.^{-1}$ band measures the acid fluoride group (—COF) in the polymer. The 1814 and 1781 $cm.^{-1}$ bands measure the free end bonded forms, respectively, of the carboxylic acid groups (—COOH). The 1800 $cm.^{-1}$ band measures the methyl ester group ,—$COOCH_3$) and the 1793 $cm.^{-1}$ band measures the perfluoro vinyl end-group (—$CF=CF_2$). The quantitative measurement of the number of these groups was obtained by measurement of the extinction coefficients of each of these groups in known compounds and comparing these coefficients with the measurements obtained for the treated copolymer. Because of

the overlapping of some of the bands it was found necessary to correct the absorbances for contributions from other groups. The end-groups are expressed as the number per one million carbon atoms in the polymer.

The stability of a fluorocarbon polymer during melt fabrication may be measured by a number of tests. A preferred test comprises the measurement of the change in melt viscosity when the polymer is exposed for a period of time to high temperatures, either in the presence or absence of oxygen. The term "specific melt viscosity" as used herein means the apparent melt viscosity as measured at 380° C. under a shear stress of 0.46 Kg/cm$^2$. Specific melt viscosity is determined by using a melt indexer of the type described in ASTM D-1238-52-T, modified for corrosion resistance to embody a cylinder, orifice, and a piston made of "Stellite" (Registered Trade Mark) cobalt-chromium-tungsten alloy. The resin is charged to the 9.53 cm. I.D. cylinder which is held at 380° C.±0.5° C. allowed to come to an equilibrium temperature during 5 minutes, and extruded through the 2.1 cm. diameter, 8.0 cm. long orifice under a piston loading of 5000 grams. The specific melt viscosity in poises is calculated as 53,150 divided by the observed extrusion rate in grams per minute. The stability of the polymer may also be measured by its volatiles index. In this test, a 10 g. sample of the resin is placed in an aluminum foil thimble, which is charged into a glass vial of volume 100 cc. attached to a vacuum system. The vial is evacuated to 2 mm. (Hg) and then on reaching an equilibrium, placed in a hot block maintained at 380° C. The change in pressure is recorded every ten minutes over a period of 60 minutes. The volatiles index V.I. is calculated using the following equation

$$\text{V.I.} = \frac{(P_{40} - P_0)V}{10 \times W}$$

where $P_{40}$ and $P_0$ are the pressures of the sample in mm Hg prior to insertion and after 40 min. in the hot block and V is the volume of the vial in cc. and W is the weight of the sample in grams.

It is preferred that the volatiles index be less than 25 because when the volatiles index is above 25 the number of bubbles formed on extrusion is detrimental to the properties of the copolymer.

The following Examples further illustrate the nature of the present invention. Parts are by weight unless otherwise indicated.

## Example I

Into a conventional one-litre stainless steel agitated pressure vessel were charged 850 ml. of 1,2,2 - trichloro - 1,1,2 - trifluoroethane ("Freon"-113 or F-113 "Freon" is a Registered Trade Mark), 14 grams of perfluoropropyl/perfluorovinyl ether (PPVE) and 20 ml. of a 0.027 gram/cc. solution of bis(perfluoropropionyl) peroxide (3P) in F-113. The pressure was maintained at 2.11 Kg/cm$^2$ g. during the polymerization by continuous addition of tetrafluoroethylene (TFE). The temperature was controlled at 50° C. by circulating water in the jacket of the autoclave and conventional control elements. After 20 minutes the polymer suspension was removed, mixed with 750 ml. of methanol and filtered through a fritted glass funnel. The gelatinous filter cake was washed with 500 ml. of methanol in an Osterizer blender and filtered. This procedure was repeated three times. The polymer was then dried for 16 hours at 130° C. in an air circulating oven. A similar polymerization run was made in which the polymer was not treated with methanol but was filtered and dried as above. Both the polymer, which had been treated with methanol (i.e. that having methyl ester end-groups) and the untreated polymer were boiled in water for 4 hours and 16 hours and the end-groups and volatiles indices were measured as described above and compared. The methanol-treated polymer maintained a low volatiles index (less than 25) throughout the test, while that of the untreated polymer markedly increased (to approximately 39). The number of methyl ester end-groups of the methyl ester capped polymer was virtually unchanged after being boiled for 16 hours.

## Example II

A polymer was prepared in a similar way to that in Example I except that a one-gallon autoclave and larger amounts of starting material, namely 5070 grams F-113, 40.1 grams PPVE and 56 ml. of a 0.08 gram/cc. solution of 3P, were used. The pressure in the vessel was maintained at 2.11 Kg/cm$^2$g. using TFE and its temperature was kept at 50° C. 1 ml. of methanol was added to approximately 1 litre of the gel so obtained and the mixture was mixed manually for several minutes, filtered on a basket centrifuge, and dried at 100° C. for 16 hours. After the polymer had been dried, a small part was extracted with water in a Soxhlet apparatus for 16 hours and then dried for 2 hours at 100° C. The volatiles index of the polymer having methyl ester end-groups was low (less than 25). End-group analysis (using the procedure used in Example I) of this polymer indicated that the ester groups were stable to the above ageing procedure.

## Example III

To a 180 ml. stainless steel tube was added 15 grams of a polymer fluff having methyl ester end-groups and a 10 mil film of a polymer having methyl ester end-groups prepared as in Example II (except that only 49

ml. of a 0.057 grams/cc. solution of 3P were used) and 90 ml. of distilled water. The tube was sealed and evacuated to remove air and then heated to 225° C. for 4 hours. The polymer fluff and film were recovered and dried 16 hours at 125° C. The end-groups on the polymer were determined both before and after the above heat treatment by infrared analysis as in Example I. Results indicated that the methyl ester end-groups remained stable during the treatment.

A polymer which had not been treated with methanol was contacted with water for 4 hours at 100° C. for comparison and its end-groups were analyzed both before and after treatment. Most of the acid fluoride end-groups were converted to carboxylic acid end-groups which caused an increase in the volatiles index.

## Example IV

The polymer for this Example was prepared as in Example I using 1340 grams F-113. 10.6 grams PPVE, and 0.60 gram 3P initiator in an autoclave maintained at a pressure of 2.11 Kg/cm²g. with TFE. The end-groups of the polymer were then converted to methyl ester groups by adding 5 ml. methanol to the dispersion of the polymer in F-113, stirring, filtering and drying overnight at 100° C. A ten-gram sample of the polymer having methyl ester end-groups was placed in a "Pyrex" (Registered Trade Mark) glass tube and inserted into an aluminium block held at 380° C. A very slight air stream was blown into the sample tube. After 15 minutes the sample was removed and the weight loss, melt viscosity at 380° C., and the number and type of end-groups were measured. The heat treatment was repeated except that treatment times of 30 and 60 minutes were used. After 15 and 30 minutes treatment the number of methyl ester end-groups in the polymer was essentially unchanged. Only after a heat treatment of 60 minutes at 380° C did the number of methyl ester end-groups become so small as to be undetectable. Only small changes were noted in the weight and melt viscosity of the sample.

Another sample of a similar polymer having methyl ester end-groups was subjected to oxidative attack by placing it in an air circulating oven at 300° C. The change in melt viscosity was very small after six hours. After 4 hours the number of methyl ester end-groups had decreased only slightly. Only after 6 hours at 300° C. were no methyl ester groups detectable.

## Example V

Each of the several batches of polymer prepared as in Example III, were treated with 10 ml. of methanol, stirred, centrifuged, treated with 2500 ml. methanol for 10 minutes, centrifuged and then dried at 125° C over night. A blend of the polymer having methyl ester end-groups so obtained was prepared and extruded four times using a 38.1 cm. extruder. The extrusion temperature was 390° C. The melt viscosity, volatiles index and end-groups were analyzed before and after each extrusion. Results indicate that the methyl ester end-groups were stable under the conditions of extrusion. Melt viscosity did not change appreciably and the volatiles index remained below 25.

The polymer used in Examples VI and VII was prepared as in Example I at Column 4, lines 23—64, in U.S. Patent Specification No. 2,946,763. It will be referred to as "FEP polymer" for convenience.

## Example VI

Twenty grams of FEP polymer, filtered but not dried, were placed in a stainless steel shaker tube of about 20 ml. total volume. 100 ml. of reagent grade methanol was added to the shaker tube which was then sealed and heated to 140° C. for 120 minutes with agitation. At the end of this heating period the cylinder was cooled to room temperature and its contents washed several times with methanol. After air drying the sample until the odour of methanol could not be detected, the sample was dried at 115° C. under vacuum overnight. Infrared analysis of films compression moulded at 340° C. showed that 225 methyl ester and 206 perfluorovinyl end-groups per $10^6$ carbon atoms were present, indicating that all carboxylic acid end-groups had been esterified.

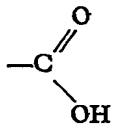
## Example VII

Twenty grams of dry FEP polymer were placed in a stainless steel shaker tube of about 200 cc. total volume. 100 ml. of reagent grade methanol was added to the shaker tube which was then sealed and heated to 190° C. for 120 minutes with agitation. At the end of this heating period the cylinder was cooled to room temperature and its contents washed several times with methanol. After air drying the sample until the odour of methanol could not be detected, the sample was dried at 115° C. under vacuum overnight. Infrared analysis of films compression moulded at 340° C. showed that 329 methyl ester and 15 perfluorovinyl end-groups per $10^6$ carbon atoms were present, indicating that all carboxylic acid end-groups had been esterified.

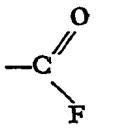
## WHAT WE CLAIM IS:—

1. Process for stabilising a copolymer of tetrafluoroethylene and another ethylenically unsaturated fluorine-substituted monomer,

which copolymer has end-groups of the formula



or



which process comprises converting at least half of said end-groups to methyl ester groups.

2. Process according to claim 1 wherein the copolymer contains carboxyl end-groups and is contacted with methyl alcohol at 65° C to 200° C.

3. Process according to claim 2 wherein the temperature is 130° to 200° C.

4. Process according to claim 1 wherein the copolymer contains acid fluoride end-groups and is contacted with methyl alcohol at 0° to 200° C.

5. Process according to claim 4 wherein the temperature is 20° to 65° C.

6. Process according to any one of the preceding claims wherein the other monomer is a fluoroolefin having the general formula

$$XCF_2(CF_2)_nCF=CF_2$$

where X represents a fluorine or hydrogen atom and n is 0 or an integer from 1 to 9; a fluorovinyl ether having the general formula

$$XCF_2(CF_2)_mOCF=CF_2$$

where X represents a fluorine or hydrogen atom and m is 0 or an integer from 1 to 7; a fluorovinyl polyether having the general formula

$$XCF_2(CF_2)_mOCF(CF_3)CF_2OCF=CF_2$$

where X represents a fluorine or hydrogen atom and m is 0 or an integer from 1 to 7; or perfluoro(2 - methylene - 4 - methyl - 1,3 - dioxolane).

7. Process according to claim 6 in which the other monomer is hexafluoropropylene.

8. Process according to claim 6 in which the other monomer is perfluoromethyl perfluorovinyl ether.

9. Process according to claim 6 in which the other monomer is perfluoroethyl perfluorovinyl ether.

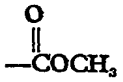
10. Process according to claim 6 in which the other monomer is perfluoropropyl perfluorovinyl ether.

11. Process according to claim 1 substantially as hereinbefore described.

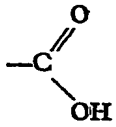
12. Process according to claim 1 substantially as described in any one of the foregoing Examples.

13. A stabilised copolymer prepared by a process as claimed in any one of the preceding claims.

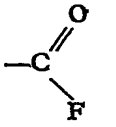
14. A copolymer of tetrafluoroethylene and another ethylenically unsaturated fluorine-substituted monomer in which, as measured by infra-red analysis, at least half of the end groups are of the formula



and remaining end groups (if any) are



or



15. A copolymer according to claim 14 wherein the other monomer is a fluoroolefin having the general formula

$$XCF_2(CF_2)_nCF=CF_2$$

where X represents a fluorine or hydrogen atom and n is 0 or an integer from 1 to 9; a fluorovinyl ether having the general formula

$$XCF_2(CF_2)_mOCF=CF_2$$

where X represents a fluorine or hydrogen atom and m is 0 or an integer from 1 to 7; a fluorovinyl polyether having the general formula

$$XCF_2(CF_2)_mOCF(CF_3)CF_2OCF=CF_2$$

where X represents a fluorine or hydrogen atom and m is 0 or an integer from 1 to 7; or perfluoro(2 - methylene - 4 - methyl - 1,3 - dioxolane).

16. A copolymer according to claim 15 in which the other monomer is hexafluoropropylene.

17. A copolymer according to claim 15 in

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which the other monomer is perfluoromethyl perfluorovinyl ether.

18. A copolymer according to claim 15 in which the other monomer is perfluoroethyl perfluorovinyl ether.

19. A copolymer according to claim 15 in which the other monomer is perfluoropropyl perfluorovinyl ether.

20. A copolymer according to any one of claims 14 to 19 which has a volatile index as hereinbefore defined of less than 25.

21. A copolymer according to claim 14 substantially as hereinbefore described.

22. A copolymer according to claim 14 substantially as described in any one of the foregoing Examples.

23. Process for the preparation of a shaped article which comprises melt-extruding a copolymer as claimed in any one of claims 13 to 22.

24. A shaped article prepared by a process as claimed in claim 23.

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